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(54) Title: TREATMENT OF DYE BATHS BY A MEMBRANE PROCESS FOR THE PURPOSE OF THE REUSE OF THE WATER AND NACI IN THE PROCESS

(57) Abstract: The present invention relates to a process for the treatment and the recovery in value of baths for the dyeing of cellulose fibres with reactive dyes comprising a prefiltration, a neutralization, a nanofiltration and a reverse osmosis. The following are reused at the end of the treatment: on the one hand, colourless water comprising the inorganic salts necessary for a new dyeing with reactive dyes; on the other hand, pure water which will be used either during the nanofiltration or for other operations, such as washing or rinsing the dyed material. Furthermore, an aqueous solution of very low volume, mainly comprising hydrolysed reactive dyes and dye additives, is recovered. This results in savings in water, in a drastic reduction in the salinity of the effluents and in a simplification in the treatment of the effluents originating from the other baths necessary for the processing of cotton dyed with reactive dyes, in short in a significant reduction in pollution of the environment.

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TREATMENT OF DYE BATHS BY A MEMBRANE PROCESS FOR THE PURPOSE OF THE REUSE OF THE WATER AND NaCl IN THE PROCESS

5   The present invention relates to a process for the treatment of baths for the dyeing of cellulose fibres with reactive dyes comprising a prefiltration, then a neutralization, then a nanofiltration and then a reverse osmosis.

10   **THE ENVIRONMENTAL PROBLEM**
Among all the fibres which are dyed today, it is the exhaustion dyeing of cotton with reactive dyes which consumes the most water and which releases, at the end of the cycle, aqueous liquors charged with the highest loads of different kinds of pollutants. Exhaustion dyeing of cotton with dyes of this category requires in total approximately
15   ten baths, which corresponds to 70 to 150 litres of water in total per kilo of material. Among these approximately ten baths, the dye bath is the most polluted, as it comprises:

-       hydrolysed dye not fixed to the material. This residual amount is
20   responsible for the unacceptable colouring of the effluents.
-       organic matter of various types acting as components in the dye additives. Their presence is reponsible for the high DCO/DBO of the effluents.
-       cotton fibrils. Their presence is responsible for the increase in the suspended matter of the effluents.
25   -   from 30 to 100 g/l of electrolytes, in fact in particular sodium chloride and sodium carbonate; these two salts are responsible for the very high salinity of the waste water. The standards relating to the salinity of waste water are today becoming increasingly strict. Thus, the overall salinity of the approximately ten baths which are necessary for the processing of the
30   cotton, mixed together, is still too high to allow discharge to rivers without having a negative impact on the life of the living organisms and plankton which populate fresh water. The same situation applies in a plant, where the activity of the bacteria present in the biochemical treatment sludges is disturbed in the presence of electrolytes.
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THE STATE OF THE ART

Today, in the majority of cases, all the baths, including the dye bath, are mixed, which increases the total volume and dilutes all the concentrations of the various pollutants. They are subsequently treated in conventional plants combining a physicochemical

5 treatment, followed by a decolorization treatment, if necessary, to finish with a biochemical treatment. Unfortunately, the salinity of the effluents at the end of such a treatment is still, and by far, greater than 1 g/l of electrolyte. This limit, relating to sodium chloride or sodium sulphate and which may or may not allow a dyeing plant to discharge its waste water to a river, is in the course of becoming, in the majority of

10 countries, the maximum limit allowed for discharge. How can compounds, which are dangerous when all is said and done, of such low molecular weights be efficiently and economically separated?

15 PRINCIPLE OF THE INVENTION

The invention consists in isolating the dye bath and in then filtering, neutralizing and treating it by nanofiltration (NF)/reverse osmosis (RO) coupling, separately, for the purpose of recovering most of the water of the bath devoid of dyes and of chemical products but with most of the salt introduced at the start of the dyeing, on the one hand,

20 and, on the other hand, a minimum volume of an aqueous solution comprising the other compounds and in particular the hydrolysed reactive dyes. The water thus obtained is reused in a new dyeing. The aim of the process is to recover in value and to treat a dyeing effluent not in order to be allowed to discharge it but in order to reuse it. This results in savings in water and in electrolytes and in a simplification of the

25 treatment of the other baths, in particular as regards the total salinity of the effluents. The part of the bath separated during the NF/RO coupling, which has a very low volume but which comprises high concentrations of components, will, in the light of its very low volume, be conveyed to a landfill site or will be sent for incineration.

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STATE OF THE ART

Among the various methods of separating inorganic and organic solutes, membrane filtration has the advantage of being efficient in terms of separation, of consuming little energy, of being able to be used continuously and to be easily automated, of offering a

35 very low dead volume and a very high specific surface area, and, finally, of carrying out the desired separation in a single stage with the addition of a third substance.

Membrane filtration can therefore advantageously replace more conventional biological or physicochemical operations used essentially for effluent treatment.

5   According to Aptel *et al.* (Procédés membranaires [Membrane processes].
Proceedings of "Environnement et électricité [Environment and electricity]", 1993,
Paris), if membrane processes are categorized by sizes of compounds to be
separated, the most commonly employed industrially are: reverse osmosis (RO = size
of the solutes: 0.1-1.2 nm); nanofiltration (NF = size of the solutes: 0.5-1.5 nm);
10   ultrafiltration (UF = size of the solutes: 1.2-500 nm) and microfiltration (MF = size of the
solutes: 500-10 000 nm).

Of these membrane filtration processes, which operate under pressure, nanofiltration
seems potentially the best candidate for separating organic molecules from inorganic
15   salts, that is to say the hydrolysed reactive dyes from the inorganic salts present, as
neither UF nor RO can separate inorganic salts from small organic molecules.

These membrane filtration processes, carried out under pressure, operate with a
tangential filtration arrangement, where the feed stream is perpendicular to the stream
20   which passes through the membrane. Operating in this way makes it possible to avoid
the accumulation of material, which increases the resistance to transfer, by flushing the
membrane surface.

In these processes, as in the description of this invention and of the claims which
25   accompany it, only a portion (permeate) of the feed solution passes through the
membrane. The feed stream which has not passed through the membrane is known as
the "retentate". The retentate can be collected directly but, in this case, to obtain a
satisfactory effectiveness, it is necessary to use large membrane surface areas (or to
repeat the operation over several successive filtration devices). The retentate can also
30   be recycled to the main tank, which is the most common and most economical
procedure, and that which will be described in this invention.

In the case of the separation of two solutes O and I (O being an organic compound and
I an inorganic salt or inorganic salts), the effectiveness of the separation process is
35   expressed by the following parameters:

Degree of retention $=(([O]_{feed} - [O]_{permeate}) / [O_{feed}]) \times 100$

The same relationship is used for the solute I.

5   Permeate flux = flow rate of the material passing through the membrane / surface area
     of the membrane. This flux, given for a given transmembrane pressure (tmp), is
     generally corrected to 20°C by taking into account the variation in the viscosity of the
     solution as a function of the temperature.

10   Filtration membranes are chemically aromatic polymers of crosslinked polyamide type
     which are deposited as a thin layer ("skin"), providing the selectivity, above a layer of
     microporous polymer (support), providing the mechanical strength, to provide a
     composite membrane structure. Such a membrane structure is commonly denoted TFC
     (thin film composite). Nanofiltration and reverse osmosis membranes are available
15   from known suppliers of reverse osmosis membranes and of other membranes which
     operate in pressurized processes. Mention may be made, for example, of the
     companies: Osmonics, Millipore, Pall or Filmtec.

     Nanofiltration and reverse osmosis membranes are typically packaged in modular form.
20   A module of "spiral-wound" type is very often employed as this type of module exhibits
     the advantages of being compact, of having a low pressure drop and a low dead
     volume, and of being reasonably priced. It is this type of module which will be used in
     the description of this invention. However, modules of another type, with a different
     configuration, such as flat membranes, can also be employed.
25
     The main applications of nanofiltration are the production of softened water or of
     ultrapure water and the selective removal of multivalent ions with respect to
     monovalent ions. For example, the removal of silica and of sulphate in brines is very
     important industrially. This is because the silica dissolved or in suspension in the brine
30   which feeds the process for the manufacture of chlorine by electrolysis (in particular the
     membrane cell process) presents a problem because it forms a coating on the surface
     of or inside the ion-exchange membrane separator. In the process for the manufacture
     of sodium chlorate, the silica, if it is present in the feed brine, also results in insoluble
     deposits on the anode, which result in an increase in the cell voltage and in premature
35   wear of the coating of the anode.

Furthermore, sulphate is a common component of commercial brine and, when specific operations are not carried out to remove it, it enters the electrolytic system, where it accumulates. With time, the concentration of sulphate increases and disrupts the electrolysis by causing operational problems due to localized precipitation in the

5   electrolysis cells. It is therefore desirable for the concentration of sulphate or of silica in the concentrated brine to be reduced as much as possible. This is why nanofiltration methods have been described for replacing conventional methods for the precipitation of the harmful salts.

10   Thus it is that Patent WO 96/33005 discloses a nanofiltration process for removing sulphate, silica and dichromate from a brine solution.
     Likewise, Patent US 5 858 240 discloses a nanofiltration process for reducing the concentration of sulphate, of silica, of dichromate or of phosphate in the feed brine of the process for the manufacture of chlorine or of the chlorate process.

15

     Furthermore, nanofiltration has been used downstream of industrial processes for extracting certain inorganic salts present in aqueous solutions. Thus it is that the thesis of Eric Gaubert (thesis) describes the separation of radioelements, of nonradioactive elements by nanofiltration assisted by complexing in a highly saline medium.

20

     K. H. Ahn *et al.* describe the removal of ions in aqueous rinsing liquors from the electrodeposition of nickel using low-pressure nanofiltration (14146746 Pascal No. 99-0343865)

25   Likewise, K. Linde *et al.* describe the nanofiltration of saline solutions originating from landfill sites (leachate) which makes it possible to retain the heavy metals, which are polyvalent cations, such as Cd, Zn, Pb or Cr, and to discharge the monovalent cations, such as Na or K, which are substances of low toxicity (Desalination, No. 103 (1995) 223).

30

     A few examples of separation between organic compounds and inorganic salts in dilute solutions are also known.

     Foster *et al.* remove chlorinated organic derivatives and pesticides from drinking water

35   by nanofiltration (J. Inst. Water Environ. 5 (1991) 466-477).

Garema *et al.* describe the standardization of the quality of milk by nanofiltration of amino acids over an organic membrane (le lait [Milk], 76 (1996), 267-281).

Trebouet *et al.* describe the treatment of leachates from landfill sites by nanofiltration
5   and ultrafiltration, in order to bring about the passage of organic molecules of moderate size at the expense of large organic molecules (not necessarily biodegradable molecules) (Rev. Sc. Eau [Sci. Rev. Water]; No. 3 (1993), 365-381).

By the side of the methods for the conventional treatment of dyeing plant effluents,
10   which combines a physicochemical treatment and/or a decolorization treatment and/or a biological treatment, there exists a real need for a method, situated at the very core of the dyeing process, which makes it possible to recycle the concentrated sodium chloride and the water, on the one hand, and to concentrate the hydrolysed reactive dyes, on the other hand.

15

In fact, it would be necessary to find a process which makes it possible to recycle a concentrated solution of sodium chloride in the maximum amount of pure water and to discharge a minimum volume of water comprising the hydrolysed reactive dyes and the dye additives.

20

It has now been found that a process comprising a prefiltration, then a neutralization, then a nanofiltration and then a reverse osmosis fulfills the requirements.

Object of the present invention is therefore a process for the treatment of baths for the
25   exhaustion dyeing of cellulose fibres with reactive dyes comprising a prefiltration, then a neutralization, then a nanofiltration and then a reverse osmosis.

The instant process is characterized in that the dye baths are industrial baths and in that they comprise hydrolysed reactive dyes which preferably belong to the
30   trichloropyrimidine, difluoropyrimidine, difluoromonochloropyrimidine, monochlorotriazine and vinyl sulphone families.

The prefiltration is carried out with a filter with a membrane having a preferred cutoff threshold of between 80 and 120 microns.

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The neutralization is carried out with acid, preferably hydrochloric acid, in the presence or absence of bubbling of air.

During the nanofiltration, the separation is carried out in an aqueous solution, on the one hand, of inorganic salts present at high concentrations, on the other hand, of hydrolysed reactive dyes having masses close to those of the cutoff threshold of the membrane.

The feed liquor is continuously introduced into a filtration module comprising a nanofiltration membrane under a positive pressure to provide a liquor which has passed through the membrane (permeate) and a liquor which has transited without passing through the membrane (retentate), the retentate being continuously directed to the feed tank.

During the nanofiltration, hydrolysed reactive dyes are concentrated upstream of the membrane and inorganic salts are removed through the membrane via a concentration step.

Also during the nanofiltration, the concentration of hydrolysed reactive dyes upstream of the membrane is kept constant by addition of pure water and inorganic salts are removed through the membrane via a diafiltration step.

The nanofiltration stage can operate
      (i) in a single step (concentration),
      (ii) in two steps (diafiltration-concentration), or
      (iii) in three steps (concentration-diafiltration-concentration),
      preferably in three steps.

In the instant process the initial concentration of inorganic salts is between 30 and 100 g/l.

In the reverse osmosis step, the feed liquor has an initial concentration of inorganic salts of between 5 and 70 g/l , preferably between 10 and 15 g/l.

The retentate from the reverse osmosis is composed of pure water comprising inorganic salts concentrated to between 3 and 8% by weight, without coloured waste

products, at a pH preferably of between 5.5 and 6, and in that it can be reused in dyeing.

5   **DETAILED DESCRIPTION OF THE PRESENT INVENTION**

The object of the present invention is to provide an innovative process which makes it possible to separate several compounds present in an aqueous solution so as to carry out the most complete recycling possible of a compound with respect to the other compounds and to recycle the greatest possible amount of water. More specifically, the

10   object of the invention consists in separating and concentrating inorganic salts, dyes and organic additives which are soluble in water. The dyes in question are reactive dyes which either become attached by virtue of a covalent bond to the cellulose or are hydrolysed and remain in the bath. A very large number of reactive dyes exist characterized by the nature of the reactive group, which are categorized better with the

15   following names, such as, for example, dichlorotriazine, monochlorodifluoropyrimidine, dichloroquinoxaline, monochlorotriazine, vinyl sulphone and the like. The inorganic salts in question are compounds having the sodium cation and the Cl^- , SO_4^{2-} or CO_3^{2-} anion. The organic additives in question are partially neutralized compounds based on polyacrylic acid, dispersions of polyethylene waxes, or sulphonated polymers.

20

The aqueous solution comprising only concentrated inorganic salts without hydrolysed reactive dyes which is thus obtained can be reused for a new dyeing. This results in savings in water and in sea salt, in a simplification of the conventional treatment of the other baths and in a drastic reduction in the salinity of the effluents. The other

25   separated part, which is low in volume and comprising the hydrolysed reactive dyes and the chemical products at high concentrations, will be readily treated conventionally (incineration or placing in a landfill site).

Within its broadest sense, the invention relates to a prefiltration-neutralization-

30   nanofiltration-reverse osmosis process.

PREFILTRATION: STAGE 1

The aim of this very important stage is to remove the cotton fibrils and other large

35   compounds which may block the membranes downstream of the process. The formation of these fibrils is intrinsic to the exhaustion dyeing technique on modern

dyeing machinery. It depends on the type of material (jersey, interlock, loop, and the like) and on the quality of the yarn, namely the mean length of the fibres and the degree of twist. The range of cutoff thresholds envisaged varies from 10 to 200 microns, preferably from 80 to 120 microns. Various prefilter tests have shown that the use of a mean cutoff threshold of 100 microns is sufficient to completely carry out this removal.

NEUTRALIZATION: STAGE 2

The aim of this stage is to neutralize the alkali salts present in the form of carbonate essentially and of sodium hydroxide, with acid, preferably hydrochloric acid, in order to convert them to sodium chloride and to carbon dioxide gas. This is because the presence of alkali salts in the water of the bath is unacceptable during the first step of the dyeing. We have shown that it is optimal to bubble air during the neutralization with hydrochloric acid in order to remove as rapidly and as completely as possible the carbon dioxide gas formed. If the pH of the water is insufficiently acidic and if CO_2 is present, sodium bicarbonate is reformed. The presence of this salt in the recycled water, which, it should be remembered, is intended for a new dyeing, will exert an undesirable holding effect, preventing the pH of the bath from reaching the values necessary for optimum fixing of the dyes and thus preventing the redyeing. This would result in losses in the yield. The water must exhibit the following characteristics:
- pH 5.5 - 6.0, TA of less than 15°F.

To sum up, the maximum volume of a concentrated solution of inorganic salts of NaCl type having to be recycled, acidic neutralization makes it possible (i) to remove the alkali salts which might harm the yield of the redyeing, (ii) to improve the permeation flux during the nanofiltration stage 3 and (iii) to return, to the head of the process, a solution with a pH very close to that of the solutions used for dyeing (preferably 5.5-6).

NANOFILTRATION: STAGE 3

To filter in two stages, a feed liquor is introduced into a filtration module comprising a membrane, under a positive pressure, to provide a liquor which has passed through the membrane (permeate) and a liquor which has passed over without passing through the membrane (retentate), and the retentate is recycled to the tank comprising the feed liquor.

The aim of this nanofiltration is, first, to keep constant and then to increase as much as possible the concentration of dye in the retentate and reduce as much as possible the concentration therein of inorganic salts; and, secondly, to obtain the greatest possible

5   concentration of inorganic salts, the lowest possible concentration of inorganic compounds (hydrolysed dyes, dye additives) and the maximum volume of water in the permeate.

The initial concentrations of the inorganic salts in the feed liquor are between 30 and

10 100 g/l. In point of fact, the prior art does not indicate examples of a separation of hydrolysed reactive dye / inorganic salts at high concentrations present in real industrial solutions at high concentrations. This is because it has been shown that the flux decreases on average by a power of 10, while the retention of salt becomes very low, when the concentration of inorganic salt increases and reaches values of 10 to

15 20% by weight per volume (M. Nystrom *et al.*; J. Membrane Science, 98 (1995), 249-262).

We have found that it is possible to efficiently separate a dye from an inorganic salt (or from several inorganic salts) when the dye belongs, for example, to the following

20 families: trichloropyrimidine, difluoropyrimidine, difluoromonochloropyrimidine, monochlorotriazine, vinyl sulphone, and when the inorganic salts are present at a high concentration of 10% by weight.

In fact, it is surprising not to have blocking of the pores of the membrane by the organic

25 compound when the size of this compound is not very different from that of the cutoff threshold of the membrane (300 and 500 daltons respectively).

In addition, the results obtained are unexpected as it might have been feared that modifications to the membrane would arise due to the ionization and to the hydration of

30 the polymer which forms this membrane, more specifically a modification by the adsorption of the hydrolysed reactive dyes on the membrane.

To sum up, the high performances obtained are surprising as there was nothing to allow it to be anticipated that chemical and/or physical blinding of the membrane could

35 be avoided in the light of the concentrations and molecular masses of the products present in the effluents to be treated.

Consequently, such an unexpected selectivity of the membrane, at a high concentration of salt, offers advantageous applications in concentrating the dyes and separating the inorganic salts, such as NaCl, present in an aqueous solution.

The dye is at a concentration of 0.01 to 4 g/l (with a preferred mean of 2 g/l); the inorganic salts are at a concentration of 1 to 100 g/l (with a preferred mean of 70 g/l).

The third stage of the process according to the invention operates at pressures of 1 to 40 bar, preferably at 10 bar, and at circulation flow rates of 100 to 600 l/h, preferably between 250 and 350 l/h. They can be carried out at any desired temperature chosen between 0°C and the boiling point of the feed liquor. However, it is limited by the temperature range recommended for the membrane (5°C to 70°C), preferably between 45 and 55°C.

At the pH defined in the neutralization stage 2, the amount of carbonates or of bicarbonates is negligable. However, for the membranes and the pH range studied, we have shown that the transfer of inorganic salts downstream of the membrane is very much reduced when the charge of these salts increases (bivalent ions). More specifically, if carbonates remain in the solution despite the neutralization, these carbonates will become concentrated upstream of the membrane and will not be recycled for redyeing.

This nanofiltration stage can be carried out in two or three stages depending on the concentration and the nature of the hydrolysed reactive dye but also on the concentration of salts. If the concentration of hydrolysed reactive dye alone is taken as basis, the following classification may be proposed:

- very low concentration of hydrolysed reactive dye: preconcentration stage
- low concentration of hydrolysed reactive dye: preconcentration - diafiltration - concentration stages
- high concentration of hydrolysed reactive dye: diafiltration - concentration

The stage of preconcentration of the dyes consists in recovering the maximum of the salts downstream of the membrane. In fact, the greater the concentration of salt upstream, the greater the amount of salts which passes through the membrane. When

the concentration of hydrolysed reactive dye becomes too great upstream of the membrane, that is to say when the permeate flux becomes too low, the diafiltration stage is begun.

5   The diafiltration stage consists in recovering the salts downstream of the membrane while operating at a constant concentration of hydrolysed reactive dye upstream. For this, pure water is added to the main reactor at a flow rate equal to the value of the permeate flow rate. The term "purified water" is understood to mean water with a concentration of inorganic salts such that the conductivity does not exceed 1 mS.cm⁻¹

10   and which is devoid of hydrolysed reactive dye. When 80 - 90% of the salt is recovered downstream of the membrane, the stage of concentrating the dyes is begun.

The concentration stage consists in concentrating the hydrolysed dyes as much as possible. This concentration stage is halted when the permeate flux becomes too low

15   or the blinding too great, more specifically when the permeate flux is approximately less than 1 $l.h^{-1}.m^{-2}.bar^{-1}$ (approximately 20% of the initial permeability of the membrane) in the case of the solutions described in this invention.

20 · REVERSE OSMOSIS: STAGE 4

This stage does not have to take place when the concentration of hydrolysed reactive dye at the beginning of stage 3 is very low. This is the case with colorations in light shades, whatever the category of reactive dyes used, or light, medium, indeed even dark, colorations produced with reactive dyes having a high degree of fixing. This is

25   because a stage of preconcentrating the dyes is sufficient. On the other hand, from the point where diafiltration is necessary, it is necessary to recover, by reverse osmosis in the permeate, the pure water introduced during the diafiltration and, in the retentate, a brine comprising as much as possible salts originating from the dye bath.

30   The aim of the reverse osmosis is therefore, on the one hand, to increase as much as possible the concentration of inorganic salts without decomposing them and, on the other hand, to obtain the purest possible water. The initial concentrations of the inorganic salts in the feed solution depend on the diafiltration stage and are between 5 and 70 g/l with a preferred mean of 10 - 15 g/l.

35

We have found that it is possible to efficiently concentrate an inorganic salt (or several inorganic salts), even when their concentrations are greater than 1% by weight.

Consequently such a selectivity of the membrane, at a high concentration of salt, offers advantageous applications in concentrating the inorganic salts present in an aqueous solution comprising inorganic salts, such as NaCl.

The fourth stage of the process according to the invention operates at pressures of 1 to 80 bar, preferably at 70 bar, and at circulation flow rates of 300 to 800 l/h, preferably at 600 l/h. It can be carried out at any desired temperature chosen between 0°C and the boiling point of the feed liquor. However, it is limited by the temperature range recommended for the membrane (5°C to 70°C). The pH used in the process according to the invention is between 5.5 and 6, a function in fact of the conditions of the second stage. The concentrations of the inorganic salts recovered in the retentate of the reverse osmosis are between 30 and 80 g/l with a mean of 60 g/l.

REDYEING TEST

These redyeing tests are not described in the process but they validate it. They are described in APPENDIX 1. These comparative redyeing tests were carried out with laboratory water, reference dyeing and a brine recycled according to the process described in the present patent. Four categories of dyes were tried out; there is no difference in behaviour of the dyes between the two aqueous systems used.

DESCRIPTIVE DIAGRAM OF THE PROCESS

PRESENTATION

In order for the invention to be better understood, the optimum processing conditions will be described using examples which refer to Figures 1-4. Figure 1 is a diagrammatic representation of the complete process described in this invention. Steps 1 and 2 are stages of pretreatment of the effluent which make it possible to carry out Stages 3 and 4 under the best possible conditions. At the outlet of these two pretreatment stages, the solution is conveyed to Stages 3 and 4, which constitute the core of this invention.

All the tests were carried out on baths originating from industrial dyeing and not on reconstituted baths. All the membrane filtration (nanofiltration and reverse osmosis) tests were carried out with membrane surface areas of between 0.4 and 5 m², preferably 2.5 m².

5

PRINCIPLE

The dyeing plant effluent is first conveyed to prefiltration in Stage 1. The object is to stop the cotton fibrils present in order to avoid blinding of the membranes in Stages 3

10   and 4. Stage 2 is a stage of neutralization of the sodium carbonates present in the solution. This neutralization is carried out with concentrated hydrochloric acid until a pH of between 5.5 and 6.0 is obtained. The effluent, thus prefiltered and neutralized, is conveyed to Stage 3. The main aim of this stage is to separate the sodium chloride salts and to concentrate the dyes. This Stage 3 is divided into 2:

15

- a diafiltration stage, where the inorganic salts are separated while keeping the concentration of dye constant by addition of purified water,
- a concentration stage, where the dye is concentrated as much as possible.

20   The term "purified water" is understood to mean water with a concentration of inorganic salts such that the conductivity does not exceed 1 mS.cm^{-1} and which is devoid of hydrolysed reactive dye. In view of its very low volume, the concentrated dyeing solution is subsequently conveyed to a landfill site or is incinerated.

25   The sodium chloride solution is conveyed to Stage 4, where it is concentrated. The concentrated sodium chloride solution is intended to be recycled at the head of the dyeing plant process. The solution of pure water obtained downstream of the reverse osmosis membrane is recycled either to Stage 3, to provide purified water necessary for the diafiltration step, or the head of the dyeing process, to provide softened water.

30

DESCRIPTIVE DIAGRAM OF STAGE 1 (PREFILTRATION)

Stage 1 is composed solely of a stainless steel prefilter, the characteristics of which are as follows: stainless steel material, cut off at 100 μm. The scheme of the prefilter is

35   given by Figure 2.

Tests on approximately 15 000 litres of industrial solutions of hydrolysed reactive dyes did not show any blinding of these prefilters and complete retention of the fibrils. This retention is demonstrated by the presence of a 70 micron safety prefilter placed downstream and comprising no cotton fibrils.

5

DESCRIPTIVE DIAGRAM OF STAGE 2 (NEUTRALIZATION)

The arrangement in Figure 3 relating to Stage 2 comprises a holding tank with a capacity of 100 litres, a stirring paddle, a pH-meter probe, a metering pump, a

10 hydrochloric acid tank and an aeration system in the vessel bottom for conveying air. The pH of the dyeing solution is continuously measured and a metering pump makes it possible to adjust the pH of the solution to a value between 5.5 and 6.0. The amount of concentrated hydrochloric acid (9.05 N or 33%) is between 5 and 35 ml/l (preferably 20 ml/l) depending on the type of effluent and on the concentration of carbonates.

15

It is found that the replacement of the carbonate by a mixture of carbonate and of sodium hydroxide is advantageous. It makes it possible to greatly reduce the amounts of hydrochloric acid necessary. We have confirmed that this mixture does not compromise the conditions of the dyeing. In fact, the final yield of the dyes and the rate

20 and the equal depth of the dyeing are not affected by this modification. As will be discovered subsequently, the acidification of the water (pH 5.5) offers a second advantage: the permeate flux during the nanofiltration is greatly improved.

carbonate in g/l	9.55N or 35% HCl in ml/l	carbonate in g/l	36°Be sodium hydroxide in ml/l	9.55N ou 35% HCl in ml/l
20*	32	10*	2*	18
15	24	8	1.5	15
10	16	6	1	11
5	8	3	0.5	5.5

25 * The dyeing behaviour of the reactive dyes in a dye bath comprising 20 g/l of carbonate is the same as that obtained in a bath comprising 10 g/l of sodium carbonate plus 2ml/l of 36°Be sodium hydroxide. In contrast, less hydrochloric acid will be used for the neutralization of the corresponding baths.

30

DESCRIPTIVE DIAGRAM OF STAGE 3

The arrangement of Figure 4 comprises a tank A made of polymethacrylate with a capacity of 25 litres which comprises the feed solution originating from Stage 2. This tank is connected to the filtration cartridge D via a feed circuit 2 made of stainless steel

5 and is adjusted in temperature by a thermostatically controlled bath which makes it possible to keep the temperature constant between 20 and 60°C. The feed circuit 2 comprises a high-pressure pump B with a variable-speed drive unit and an emptying circuit 5 with a valve C which are situated before the pump B.

10 The filtration cartridge D, composed of a cylinder made of epoxy glass polymerized under hot conditions, comprises a membrane of spiral-wound geometry. The membrane is of organic type, made of polyamide/polysulphone, with an exchange surface area of 2.5 m^2. This nanofiltration membrane is sold by Osmonics under the generic term Desal 5. The permeate which passes through the membrane is directed to

15 receiver H.

The retentate is recovered via the circuit 3 and passes through a control valve E to be recycled to the tank A. To keep the volume of starting solution constant and to restrict blinding of the membrane, an amount of purified water equal to the volume of the

20 permeate removed is optionally added (diafiltration stage) to the tank A. This water is withdrawn from the tank G, maintained at the same temperture T as that of the fluid which circulates in 2, and is transferred to the tank A using the pump F via the circuit 4. The choice of this optional addition of water is explained by the presence or absence of a high concentration of hydrolysed reactive dyes (cf. summary and

25 description of the invention).

The circuit is also equipped with pressure sensors P_1 and P_2 which make it possible to measure the pressure drop (P_1-P_2) and the transmembrane pressure (tmp = $(P_1 + P_2)/2$) at the terminals of the membrane module. Furthermore, a conductimetry

30 electrode placed in the tank A makes it possible to continuously monitor the conductivity of the retentate over time.

When the conductivity in the tank A reaches the value corresponding to the minimum concentration of sodium salt desired, the diafiltration (the addition of water from G) is

35 halted and the filtration operation is continued, which is reflected by the decrease in the weight of retentate in A. When the weight of concentrated retentate in A is only 1/10 to

1/40 of the initial mass, the filtration operation is halted and the solutions are analysed. This range of final retentate weights makes it possible to operate with a permeate flux which is not too low, that is to say without significantly blinding the membrane. In view of its very low volume, the concentrated dye solution will be easily treated

5 conventionally (incineration or placing in a landfill site). The NaCl solution recovered in the tank H is conveyed to Stage 4 of the process.

DESCRIPTIVE DIAGRAM OF STAGE 4: REVERSE OSMOSIS PROCESS

10 The arrangement of Figure 5 comprises a tank A" made of polymethacrylate with a capacity of 20 litres which comprises the permeate originating from Stage 3. This tank is connected to the filtration cartridge D" via a feed circuit 2 made of stainless steel and is adjusted in temperature by a thermostatically controlled bath which makes it possible to keep the temperature constant between 20 and 60°C. The feed circuit 2 comprises

15 a high-pressure pump P" and an emptying circuit 5 with a valve C" which are situated before the pump P".

The filtration cartridge D", composed of a cylinder made of stainless steel, comprises a membrane of spiral-wound geometry. The membrane is of organic type, made of

20 polyamide/polysulphone, with an exchange surface area of 2.3 m^2. This reverse osmosis membrane is sold by Osmonics under the generic term SC2540C.

The circuit is also equipped with pressure sensors P$_1$ and P$_2$ which make it possible to measure the pressure drop (P$_1$-P$_2$) and the transmembrane pressure (tmp =

25 (P$_1$ + P$_2$)/2) at the terminals of the membrane module. Furthermore, a conductimetry electrode placed in the tank A" makes it possible to continuously monitor the conductivity of the retentate over time.

The permeate which passes through the membrane is recycled to the receiver G of the

30 nanofiltration operation, to provide for the diafiltration or is used as production water in dyeing. The retentate is recovered via the circuit 3 and passes through a control valve E" to be recycled to the tank A".

When the conductivity in the tank A" reaches the value corresponding to the maximum

35 concentration of sodium salt desired, the concentrating is halted. The concentrated

retentate solution is conveyed to the head of the process to carry out a new dyeing, with or without addition of topping-up salts.

Stages 1 and 4 can operate continuously or noncontinuously. On the other hand, because of the bubbling step and the concentration step in Stages 2 and 3 respectively, the latter operate very well noncontinuously.

The following examples illustrate the invention without, however, limiting it. For all the examples below, the prefiltration is carried out with a stainless steel prefilter, the characteristics of which are as follows: stainless steel material, cut off at 100 μm. A few examples are given in detail in the text and all of these examples are combined in the tables in Appendix 2. Redyeing tests are also presented in order to show the final advantage of the present invention without, however, forming part of the said invention.

STAGE 2: NEUTRALIZATION EXAMPLES

EXAMPLE 1: (WITHOUT BUBBLING OF AIR)

A synthetic solution representing a dye bath comprises 50 g/l of sodium chloride and 5 g/l of sodium carbonate. A volume of 9.4 ml/l of hydrochloric acid (33%) has to be added to this solution to obtain a pH of 5 and a total alkalinity of 2.73, thus making it possible to have a concentration of HCO_3^- of 0.546 mmol/l and of free CO_2 of 2.903 mmol/l.

EXAMPLE 2: (INFLUENCE OF THE BUBBLING OF AIR)

The same synthetic solution as in Example 1 is used but this time, after having added the same volume of hydrochloric acid, air is introduced using an aeration system. The pH of the solution is now 7.37 and the total alkalinity is 2.545, thus making it possible to have a concentration of HCO_3^- of 1.018 mmol/l and of free CO_2 of 0.032 mmol/l.

EXAMPLE 3: (WITHOUT BUBBLING OF AIR)

A synthetic solution representing a dye bath comprises 80 g/l of sodium chloride and 12 g/l of sodium carbonate. It is necessary to add a volume of 22 ml/l of hydrochloric acid (33%) to this solution to obtain a pH of 5 and a total alkalinity of 7.86, thus making

it possible to have a concentration of HCO_3^- of 1.5 mmol/l and of free CO_2 of 2.25 mmol/l.

EXAMPLE 4: (INFLUENCE OF THE BUBBLING OF AIR)

The same synthetic solution as Example 5 is used but this time, after having added the same volume of hydrochloric acid, air is introduced using an aeration system. The pH of the solution is now 7.25 and the total alkalinity is 6.495, thus making it possible to have a concentration of HCO_3^- of 1.3 mmol/l and of free CO_2 of 0.3 mmol/l.

STAGE 3: NANOFILTRATION

EXAMPLE 1

The bath to be treated originates from the industrial dyeing of 250 kilograms of pure cotton knitwear in a bath ratio of 1:6.5, i.e. a volume of 1625 litres. The starting format is as follows:

> 2.565% Drimarene Golden Yellow K-2R, i.e. 3.93 g/l
> 2.700% Drimarene Red K-8B, i.e. 4.14 g/l
> 0.050% Drimarene Blue K-2RL, i.e. 0.076 g/l
> Additive based on ethoxylated fatty alcohol 1 g/l
> Sodium chloride 80 g/l
> Sodium carbonate 8 g/l

For qualitative reasons, it is impossible to empty a dye machine directly without having cooled the material beforehand and reducing the pH by supplying fresh water. It is at this stage that the dye bath was withdrawn for the nanofiltration tests. A mass of 9000 g of a solution corresponding to the bath described above and comprising 61 g/l of sodium chloride is prefiltered with a 100 µm prefilter to remove the cotton fibrils. This solution is subsequently neutralized with a volume of hydrochloric acid (33%) of 4.9 ml/l.

The resulting solution is placed in a tank and is maintained at a temperature of 50°C. The circulation flow rate of the retentate is adjusted to 300 l/h. The transmembrane pressure is brought to 10 bar. The permeate is collected continuously. A constantly

20

identical flow rate of distilled water at 50°C is added to the tank in order to operate at a constant concentration of hydrolysed dyes: this stage is the diafiltration.

5   The conductivity of the downstream and upstream solutions is measured continuously by a conductimeter. The membrane used is a spiral membrane made of polypropylene from Osmonics with a filtering surface area of 2.5 m^2 and with a cutoff threshold of between 200 and 300 Da.

10   At the end of the diafiltration operation with a duration of 18 minutes, a concentration stage is carried out (the addition of distilled water is halted and the dyes remaining in the retentate were concentrated) with a total duration of 2 minutes. 39 800 g of permeate with a mean composition of 14 g/l of NaCl are recovered. Moreover, 1400 g of retentate with a composition of 5.7 g/l of NaCl remain in the feed tank.

15   The degree of instantaneous retention of NaCl varies from 0 to 27% within a concentration range from 61 to 5.7 g/l. The permeate recovered is colourless and transparent throughout the operation as the degree of retention of the hydrolysed reactive dyes is 99%. 91% of the sodium chloride is finally recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 1%.

20   The permeate flux varies from 40 to 51 l/h.m^{-2} during the diafiltration phase and from 51 to 39 l/h.m^{-2} during the concentration phase. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions.

25

EXAMPLE 2

A mass of 9477 g of a solution corresponding to the bath described above and comprising 61 g/l of sodium chloride is prefiltered with a 100-μm prefilter to remove the cotton fibrils. This solution is subsequently neutralized with a volume of hydrochloric

30   acid (33%) of 4.9 ml/l. A filtration operation is carried out under conditions identical to those of Example 1, apart from the fact that the transmembrane pressure is brought to 20 bar. At the end of the diafiltration operation, of a duration of 9 minutes, and the operation for concentration of the dyes, with a total duration of 1 minute, 35 509 g of permeate with a mean composition of 18 g/l of NaCl are recovered. Moreover, 4452 g

35   of retentate with a composition of 5.55 g/l of NaCl remain in the feed tank. The degree of instantaneous retention of NaCl varies from 6 to 19% within a concentration range of

61 to 5.55 g/l. The permeate recovered is colourless and transparent throughout the operation as the degree of retention of the hydrolysed reactive dyes is 99%. 92% of the sodium chloride is finally recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 1%. The permeate flux varies from
5   49 to 55 l/h.m^{-2} during the diafiltration step and from 55 to 53 l/h.m^{-2} during the concentration step. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions.

10   **EXAMPLE 3**

A mass of 9220 g of a solution corresponding to the bath described above and comprising 61 g/l of sodium chloride is prefiltered with a 100-μm prefilter to remove the cotton fibrils. This solution is subsequently neutralized with a volume of hydrochloric acid (33%) of 4.9 ml/l. A filtration operation is carried out under conditions identical to
15   those of Example 1, apart from the fact that <u>the transmembrane pressure is brought to 5 bar</u>. At the end of the diafiltration operation, with a duration of 35 minutes, and the operation of concentrating the dyes, with a total duration of 1 minute, 50 696 g of permeate with a mean composition of 11.5 g/l of NaCl are recovered. Moreover, 883 g of retentate with a composition of 6.14 g/l of NaCl remain in the feed tank. The degree
20   of instanteneous retention of NaCl varies from 0 to 40% within a concentration range of 61 to 6.14 g/l. The permeate recovered is colourless and transparent throughout the operation as the degree of retention of the hydrolysed reactive dyes is 99%. 92% of the sodium chloride are finally recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 10%. The permeate flux varies
25   from 18 to 28 l/h.m^{-2} during the diafiltration phase and from 28 to 27 l/h.m^{-2} during the concentration phase. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions.

30   **EXAMPLE 4**

A mass of 9399 g of a solution corresponding to the bath described above and comprising 60 g/l of sodium chloride is prefiltered with a 100-μm prefilter to remove the cotton fibrils. This soluton is subsequently neutralized with a volume of hydrochloric acid (33%) of 4.9 ml/l. A filtration operation is carried out under conditions identical to
35   those in Example 1, apart from the fact that <u>the circulation flow rate of the retentate is adjusted to 100 l/h</u>. At the end of the diafiltration operation, with a duration of

26 minutes, and the operation of concentrating the dyes, with a total duration of 2 minutes, 54 418 g of permeate with a mean composition of 10.8 g/l of NaCl are recovered. Moreover, 1997 g of retentate with a composition of 5.7 g/l of NaCl remain in the feed tank. The degree of instantaneous retention of NaCl varies from 5 to 25% within a concentration range from 61 to 5.7 g/l. The permeate recovered is colourless and transparent throughout the operation as the degree of retention of the hydrolysed reactive dyes is 99%. 92% of the sodium chloride are finally recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 5%. The permeate flux varies from 40 to 53 l/h.m^{-2} during the diafiltration phase and from 53 to 50 l/h.m^{-2} during the concentration phase. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions.

EXAMPLE 5

A mass of 9467 g of a solution corresponding to the bath described above and comprising 61 g/l of sodium chloride is prefiltered with a 100-μm prefilter to remove the cotton fibrils. This solution is subsequently neutralized with a volume of hydrochloric acid (33%) of 4.9 ml/l. A filtration operation is carried out under conditions identical to those of Example 1, apart from the fact that tap water is used instead of distilled water during the diafiltration (0.395 mS/cm). At the end of the diafiltration operation, with a duration of 22 minutes, and the operation of concentrating the dyes, with a total duration of 2 minutes, 54 663 g of permeate with a mean composition of 11 g/l of NaCl are recovered. Moreover, 3237 g of retentate with a composition of 4.8 g/l de NaCl remain in the feed tank. The degree of instantaneous retention of NaCl varies from 12 to 23% within a concentration range from 61 to 4.8 g/l. The permeate recovered is colourless and transparent throughout the operation as the degree of retention of hydrolysed reactive dyes is 99%. 93% of the sodium chloride are finally recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 8%. The permeate flux varies from 23 to 28 l/h.m^{-2} during the diafiltration phase and from 28 to 26 l/h.m^{-2} during the concentration phase. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions.

STAGE 4: REVERSE OSMOSIS

EXAMPLE 1

The bath to be treated originates from the dyeing of 200 kilos of pure cotton knitwear
in a bath ratio of 1:8, i.e. a volume of 1600 litres. The formula is as follows:

     0.8% Drimarene Blue HF-RL, i.e. 1 g/l

     0.312% Drimarene Red HF-G, i.e. 0.39 g/l

     0.520% Drimarene Yellow HF-R, i.e. 0.65 g/l

     Sulphonated polymer 1 g/l

     Sodium chloride 80 g/l

     Sodium carbonate 12 g/l

A mass of 14 360 g of a concentration of 25.8 g/l of the permeate originating from the
nanofiltration of this dye bath is introduced into a tank as retentate and is maintained at
a temperature of 40°C. The circulation flow rate of the retentate is adjusted to 400 l/h.
The transmembrane pressure is brought to 50 bar. The conductivity of the downstream
and upstream solutions is measured continuously by a conductimeter. The membrane
used is a spiral membrane from Osmonics with a filtering surface area of 2.5 m². A
stage of concentrating the salts is carried out with a duration of 15 minutes. 8178.2 g
of permeate with a mean composition of 2.26 g/l of NaCl are recovered. Furthermore,
5247 g with a composition of 57.36 g/l of NaCl remain in the feed tank. The degree of
instantaneous retention of NaCl varies from 97.57 to 86.44% within a concentration
range from 31.75 to 57.36 g/l. 81.23% of the sodium chloride are recovered with a
material balance confirmed to within a relative accuracy of the measurements of less
than 14%. The permeate flux varies from 26 to 4.5 l/h.m⁻². The membrane module is
fully regenerated at the end of the handling by simple acid/base washing under hot
conditions.

EXAMPLE 2

A mass of 14 439 g of a concentration of 24.8 g/l of the permeate originating from the
nanofiltration of the same dye bath mentioned in Example 1 is introduced into a tank as
retentate and is maintained at a temperature of 40°C. The circulation flow rate of the
retentate is adjusted to 400 l/h. The transmembrane pressure is brought to 50 bar. The
conductivity of the downstream and upstream solutions is measured continuously by a

conductimeter. The membrane used is a spiral membrane from Osmonics with a filtering surface area of 2.5 m^2 but tighter than the preceding one. A stage of concentrating the salts is carried out with a duration of 20 minutes. 7955 g of permeate with a mean composition of 1.37 g/l of NaCl are recovered. Furthermore, 5024 g with a

5 composition of 57.45 g/l of NaCl remain in the feed tank. The degree of instantaneous retention of NaCl varies from 98.08 to 85.87% within a concentration range from 26.88 to 57.45 g/l. 80.6% of the sodium chloride is recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 19%. The permeate flux varies from 20.52 to 1.85 $l/h.m^{-2}$. The membrane module is fully

10 regenerated at the end of the handling by simple acid/base washing under hot conditions.

EXAMPLE 3

15 A mass of 14 161 g of a concentration of 26.3 g/l of the permeate originating from the nanofiltration of the dye bath mentioned in Example 1 is introduced into a tank as retentate and is maintained at a temperature of 40°C. The circulation flow rate of the retentate is adjusted this time to 600 l/h. The transmembrane pressure is brought to 50 bars. The conductivity of the downstream and upstream solutions is measured

20 continuously by a conductimeter. The membrane used is the same as that in Example 2. A stage of concentrating the salts is carried out with a duration of 16 minutes. 7975 g of permeate with a mean composition of 1.046 g/l of NaCl are recovered. Furthermore, 5287.4 g with a composition of 57.98 g/l of NaCl remain in the feed tank. The degree of instantaneous retention of NaCl varies from 98.1 to 90.45%

25 within a concentration range from 29.07 to 57.97 g/l. 82.30% of the sodium chloride is recovered with a material balance confirmed to within a relative accuracy of the measurements of less than 15%. The permeate flux varies from 23.16 to 2.6 $l/h.m^{-2}$. The membrane module is fully regenerated at the end of the handling by simple acid/base washing under hot conditions. A summary of all the tests carried out is given

30 in Appendix 2.

APPENDIX 1

REACTIVE DYES - DYEING WITH A RECYCLED BRINE

5 1) **Aim of the test**

To confirm that a brine obtained by prefiltration (neutralization) and
nanofiltration/reverse osmosis of a dye bath of reactive dyes can be reused for a
new dyeing.

10 2) **Dye bath formula**

0.590% Drimarene Yellow HF-R

1.400% Drimarene Red HF-G

0.900% Navy HF-B

50 g/l sea salt

15 15 g/l sodium carbonate

dye additives

- After the following sequence of treatments: prefiltration, neutralization,
nanofiltration and reverse osmosis carried out with a dye bath of reactive
20 dyes, a brine is recovered which has the following characteristics:
- sodium chloride: 61 g/l ± 0.2 g/l
- pH = 5.15
- TA = 6.5
- In the tests which follow, this recycled brine will be regarded as comprising
25 60 g/l of sodium chloride.
- An IR spectrum of the brine shows that it no longer comprises dye
additives.
- The brine is colourless.
- Laboratory water used as reference:

30

- permanent hardness 0°F
- TA= less than 5
- pH= 7 ± 0.5

3) **Redyeing with Drimarene CL**

-   Material: 15 g

-   Process: Bath ratio: 1:10; total volume: 150 ml

5   With recycled brine

dye

alkali salt

With laboratory water

10   NaCl

dye   alkali salt
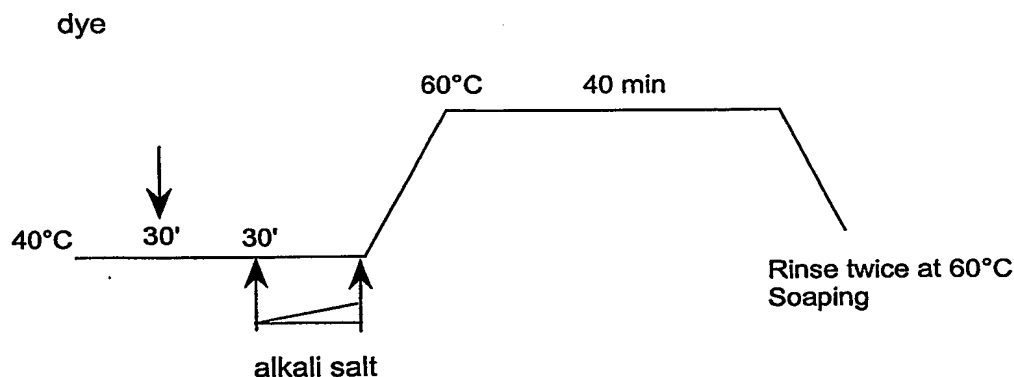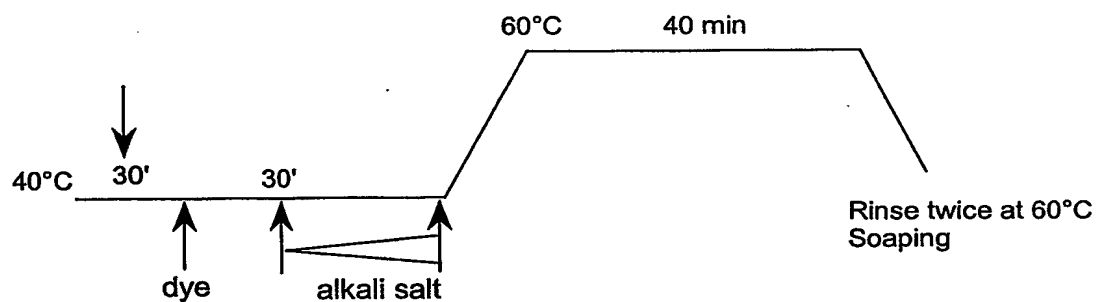
a) **Formulas with 1% of Drimarene Red CL-5B**

With laboratory water

15   1% Drimarene Red CL-5B

48 g/l sodium chloride

7 g/l sodium carbonate

With 80% recycled brine and 20% laboratory water

1% Drimarene Red CL-5B

20   no salt

·   7 g/l sodium carbonate

27

In the total volume, 48 g/l of salt originating from the recycled brine part are recovered, an amount necessary to dye 1% of Drimarene Red CL-5B.

b) Formulas with 3% of Drimarene Red CL-5B

With laboratory water

3% Drimarene Red CL-5B

70 g/l sodium chloride

12 g/l sodium carbonate

With 100% recycled brine

3% Drimarene Red CL-5B

10 g/l sodium chloride

12 g/l sodium carbonate

Use is made of 100% of recovered brine, to which 10 g/l of sodium chloride are added for the purpose of reaching the concentration of 70 g/l of electrolyte necessary for the dyeing of 3% of Drimarene Red CL-5B.

c) Results: whatever the water used, no difference (intensity, shade, fastnesses) between the colorations produced with laboratory water or recycled brine.

4) **Redyeing with Drimarene K**

- Material: 15 g
- Process: Bath ratio: 1:10; total volume: 150 ml

With recycled brine

dye

Rinse twice at 60°C
Soaping

alkali salt

28

With laboratory water

NaCl

5

a)   <u>Formulas with 4% of Drimarene Red K-4BL</u>

     With laboratory water

         4% Drimarene Red K-4BL

10   60 g/l sodium chloride

         5 g/l sodium carbonate or 3 g/l carbonate + 0.5 ml/l 36°Be NaOH

     With 100% recycled brine

         4% Drimarene Red K-4BL

         no salt

15   5 g/l sodium carbonate or 3 g/l carbonate + 0.5 ml/l 36°Be NaOH

It is pointless to add electrolyte as the recycled brine already comprises 60 g/l of sodium chloride, the amount recommended for dyeing 4% of Drimarene Red K-4BL.

20

b)   <u>Results:</u> no difference (intensity, shade, fastnesses) between the colorations produced with laboratory water or recycled brine.

5)   <u>Redyeing with Drimarene HF</u>

25   -   Material: 15 g

     -    Process: Bath ratio: 1:10; total volume: 150 ml

With recycled brine

dye

With laboratory water

NaCl

a) Formulas with 2% of Drimarene Red HF-2B

With laboratory water

2% Drimarene Red HF-2B

70 g/l sodium chloride

10 g/l sodium carbonate or 5 g/l carbonate + 1 ml/l 36°Be NaOH

With 100% recycled brine

2% Drimarene Red HF-2B

10 g/l sodium chloride

10 g/l sodium carbonate or 5 g/l carbonate + 1 ml/l 36°Be NaOH

It is necessary to add 10 g/l of electrolyte to the dye bath comprising the recycled brine instead of 70 g/l of sodium chloride, the amount recommended for dyeing 2% of Drimarene Red HF-2B.

30

b)   Results: no difference (intensity, shade, fastnesses) between the
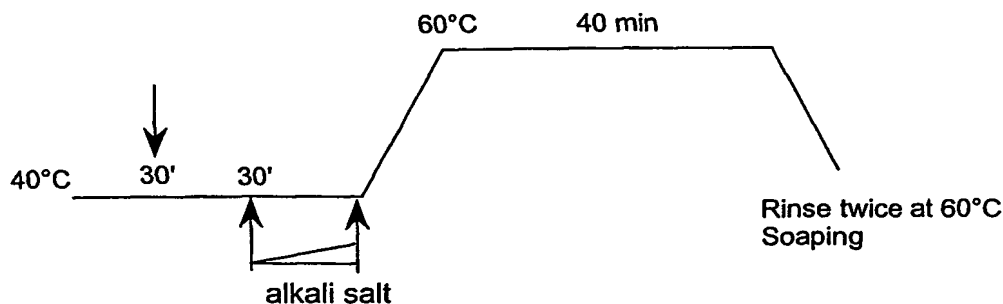colorations produced with laboratory water or recycled brine.

5

6)   **Redyeing with Drimarene XN**

-    Material: 15 g
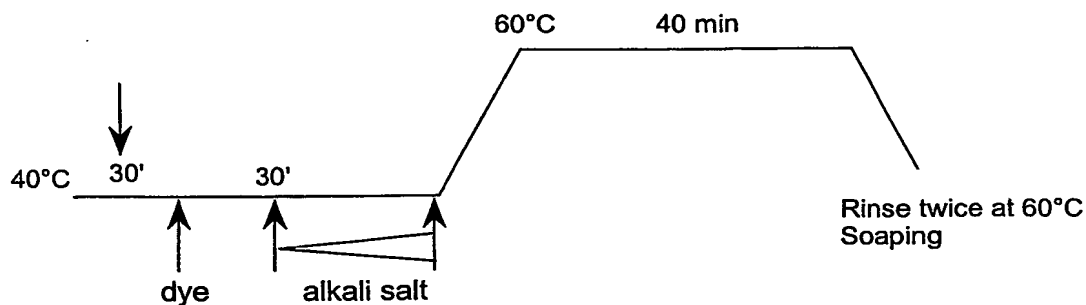
10   -   Process: Bath ratio: 1:10; total volume: 150 ml

With recycled brine

dye

98°C   40 min

60°C   30'   30'

Rinse twice at 60°C
Soaping

alkali salt

15

With laboratory water

NaCl

98°C   40 min

60°C   30'   30'

Rinse twice at 60°C
Soaping

dye   alkali salt
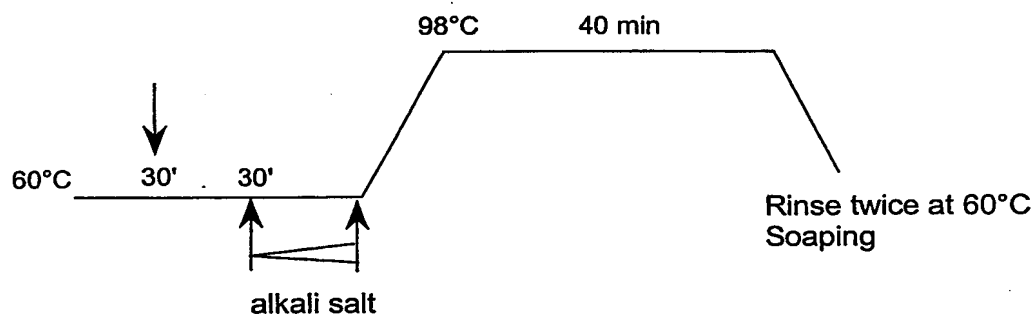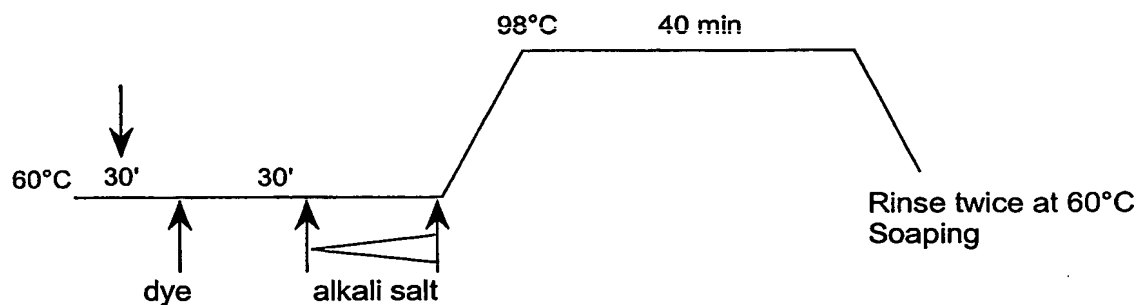
20

a)   <u>Formulas with 3% of Drimarene Yellow X-4RN</u>

With laboratory water

3% Drimarene Yellow X-4RN

70 g/l sodium chloride

15 g/l sodium carbonate or 8 g/l carbonate + 1.5 ml/l 36°Be NaOH

With 100% recycled brine

3% Drimarene Yellow X-4RN

10 g/l sodium chloride

15 g/l sodium carbonate or 8 g/l carbonate + 1.5 ml/l 36°Be NaOH

It is necessary to add 10 g/l of electrolyte to the dye bath comprising the recycled brine instead of 70 g/l of sodium chloride, the amount recommended for dyeing 3% of Drimarene Yellow X-4RN.
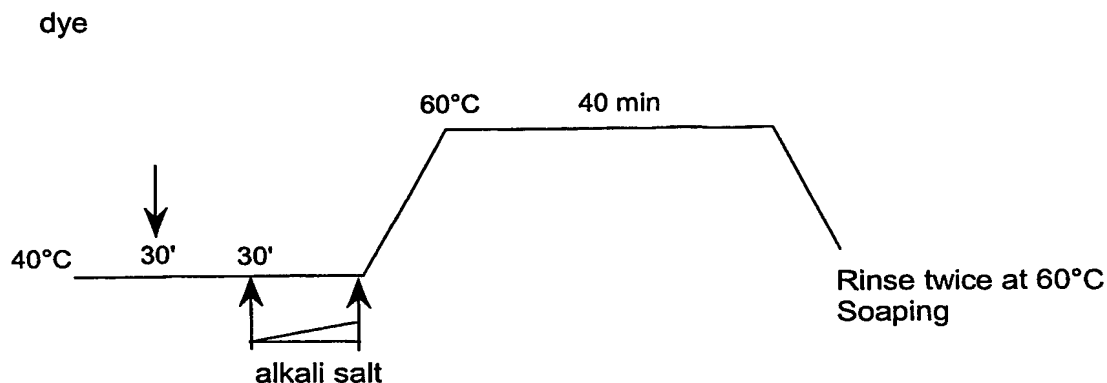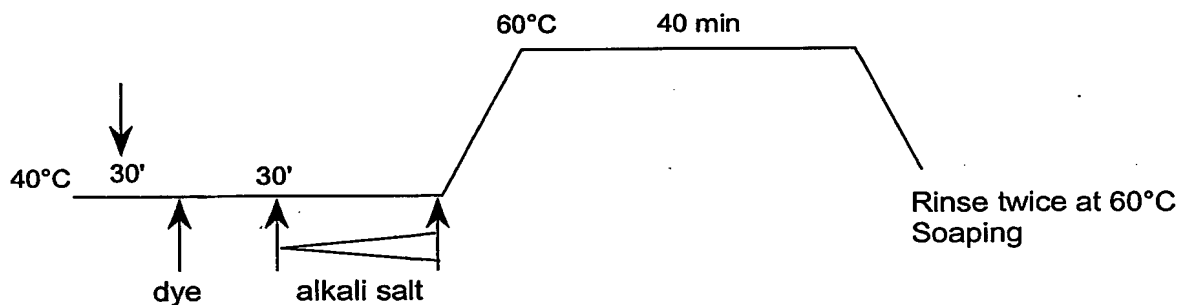
b)   <u>Results:</u> no difference (intensity, shade, fastnesses) between the colorations produced with laboratory water or recycled brine.

GENERAL CONCLUSIONS

The tests demonstrate that it is possible to use a brine recovered from an industrial dye bath comprising reactive dyes which have been subjected to the following treatment, namely prefiltration - neutralization - nanofiltration - reverse osmosis. Standard dyeings carried out with water referred to as "laboratory water" give results identical to those produced with recycled brine, after readjustment of the amount of electrolyte when this proves to be necessary. The usual fastnesses, tone and intensity are identical, whatever type of water used.

APPENDIX 2

No. of the experiments / No. Membrane	Comments	Date	Characteristics of the solutions					Neutralization stage			
			Name	Vol. (l)	Initial composition	[NaCl]o (g/l)	Absorb λ	V_{acid} (ml) (per 1 litre)	pH_{int}	pH_{fin}	TA
1 Nanomax 50		17/09/01	Drimarene X/NaCl	6.23	1.130 g/l Drimarene Yellow X-4RN 2.435 g/l Drimarene Red X-6BN 0.568 g/l Drimarene Blue X-3LR 1.500 ml/l sulphonated polymer 1.000 ml/l Sandopur R3C 1.000 ml/l Drimagen E-2R 80.00 g/l NaCl 20.00 g/l sodium carbonate	75		18	10.42	7.06	
2 Nanomax 50		20/09/01	idem	6	idem	73.74		18	10.42	7	
3 Nanomax 50		26/09/01	Drimarene K/NaCl	6.25	1 g/l ethoxylated fatty alcohol Drimarene Yellow K-2R 3.93 g/l Drimarene Red K-8B 4.14 g/l Drimarene Blue K-2RL 0.076 g/l 80 g/l NaCl 8 g/l sodium carbonate	58.1		4.2	9.64	6.85	
4 Nanomax 50		28/09/01	idem	5.78	idem	62.76		5	9.57	6.9	

5	no permeate	01/10/01	Vinyl sulphone and sulphate	5.56	2.09 g/l Remazol Black B 1 g/l Remazol Red RB 0.108 g/l Remazol Yellow RR 1.5 g/l sulphonated polymer 1 g/l Sandopur R3C 1 g/l Drimagen E-2R 5 ml/l 30°Be NaOH 5 g/l sodium carbonate 80 g/l sodium sulphate		6.8	12	6.77
6 Pall Filtron	pink permeate	02/10/01	idem	9.87	idem	85	6.4	11.99	7.05
7 Osmonics GE	nothing passes	02/10/01	idem	10	idem	85	7	12	7
8 Osmonics Desal 5 DL		09/10/01	Drimarene K/NaCl	9.93	1 g/l ethoxylated fatty alcohol Drimarene Yellow K-2R 3.93 g/l Drimarene Red K-8B 4.14 g/l Drimarene Blue K-2RL 0.076 g/l 80 g/l NaCl 8 g/l sodium carbonate	60.83	4.6	9.62	7.05
9		10/10/01	idem	9.59	idem	56	4.4	9.52	7.1

No.	Note	Date	Type		Composition					
10		11/10/01	Drimarene X/NaCl	5.82	1.130 g/l Drimarene Yellow X-4RN 2.435 g/l Drimarene Red X-6BN 0.568 g/l Drimarene Blue X-3LR 1.500 ml/l sulphonated polymer 1.000 ml/l Sandopur R3C 1.000 ml/l Drimagen E-2R 80.00 g/l NaCl 20.00 g/l sodium carbonate	70.1		19.4	10.42	7
11		12/10/01	Drimarene K/NaCl	9.22	1 g/l ethoxylated fatty alcohol Drimarene Yellow K-2R 3.93 g/l Drimarene Red K-8B 4.14 g/l Drimarene Blue K-2RL 0.076 g/l 80 g/l NaCl 8 g/l sodium carbonate	61.82		5	9.6	7.06
12		17/10/01	Drimarene K/NaCl	10	idem	60		5.07	9.6	7.08
13	poor diafiltration	17/10/01	idem	10	idem	59.67		5.3	9.61	7.09
14	tap water	18/10/01	idem	9.47	idem	61.7		5.2	9.62	6.96
15		24/10/01	idem	9.57	Idem	71.46		5.2	9.62	7.04
16		26/10/01	Drimarene HF/NaCl	10.1	Drimarene Yellow HF-R 0.09 g/l Drimarene Red HF-G 0.59 g/l Drimarene Blue HF-RL 0.80 g/l Drimagen E2R 1 g/l 65 g/l NaCl 10 g/l sodium carbonate	65.97		7.3	10.46	7.03

17		07/11/01	idem	20.46	idem	63		7.2	10.41	7.08
18		09/11/01	idem	19.29	idem	67		7.2	10.42	7
19	yellow permeate	20/03/02	Drimarene SN/NaCl	9.7	0.3% ethoxylated fatty alcohol 15 g/l Drimarene Black SN 150 powder 100 g/l NaCl 3 g/l sodium carbonate 4 g/l 30.5% NaOH	92		6.08	11.35	5.88
20		21/03/02	Drimarene K/NaCl	9.62	Drimarene Orange K-GL 1.09 g/l Drimarene Red K-8B CDG 0.58 g/l Drimarene Blue K-2RL CDG 0.89 g/l 60 g/l NaCl 5 g/l sodium carbonate	47		7.69	9.57	5.84
21		22/03/02	Drimarene SN/NaCl	9.7	0.3% ethoxylated fatty alcohol 15 g/l Drimarene Black SN 150 powder 100 g/l NaCl 3 g/l sodium carbonate 4 g/l 30.5% NaOH	90.5		4.92	11.25	5.75
22	Preconcentration in order to recover the maximum of salts	08/04/02	Drimarene HF/NaCl	300	1 g/l Drimarene Blue HF-RL 0.39 g/l Drimarene Red HF-G 0.65 g/l Drimarene Yellow HF-R 80 g/l NaCl 12 g/l sodium carbonate	81.5		9.69	9.45	6.15

23	distilled water	08/04/02	Drimarene HF/NaCl Preconcentrated	25	idem	79.6		idem	idem	idem
24	distilled water	22/05/02	Drimarene HF/NaCl Preconcentrated	15	idem	77	2.075 0.015 7.8 (609.5)	idem	idem	idem
25	ultrafiltered water	24/05/02	idem	15	idem	80.37	0.42 0 1.16 (609.5)	idem	idem	idem
26	distilled water	28/05/02	idem	25	idem	80.85	0.18 0 0.425 (609.5)	idem	idem	idem
27	ultrafiltered water	30/05/02	idem	15	idem	83.13	2.11 0 7.96 (609.5)	idem	idem	idem
28	tap water	30/05/02	idem	15	idem	81.45	0.467 0 1.524 (609.5)	idem	idem	idem

No.	Notes	Date			Colorant			
29		10/06/02	Drimarene HF/NaCl	150	0.79 g/l Drimarene Yellow HF-R 1.86 g/l Drimarene Red HF-G 1.25 g/l Drimarene Navy HF-B 50 g/l NaCl 15 g/l sodium carbonate	51.56		4.6
30	Preconcentration in order to recover the maximum of salt	11/06/02	Drimarene K/NaCl	300	1.33 g/l Drimarene Yellow K-2R CDG 2.6 g/l Drimarene Red K-8B CDG 50 g/l NaCl 5 g/l sodium carbonate	44	0.279 0 1.598 (517)	4.6
31		13/06/02	Drimarene K/NaCl	25	1.000% Drimarene Yellow K-2R CDG 1.950% Drimarene Red K-8B CDG 50 g/l NaCl 5 g/l sodium carbonate concentrated	45		3.9
32 Membrane SC 2540	Permeate of this solution obtained after diafiltration and concentration of this preconcentrated colorant	20/06/02	Drimarene HF/NaCl	14.36	1 g/l Drimarene Blue HF-RL 0.39 g/l Drimarene Red HF-G 0.65 g/l Drimarene Yellow HF-R 80 g/l NaCl 12 g/l sodium carbonate	25.8		

33 Membrane AD2540FF		02/07/02	idem	14.439	idem	24.78			
34 Membrane AD2540FF		03/07/02	idem	14.161	idem	26.3			

- CC: Concentrated Colorant
- CB: Concentrated Brine
- B: Brine
5 - PW: Purified Water

* means a footnote
l means that the figure which is not within brackets is a volume
g/l means that the figure which is within brackets is a concentration

10
In the case of the nanofiltration, the concentrated colorant is the aqueous solution comprising the hydrolysed reactive dyes, the additives and the inorganic salts which have not passed through the membrane. The concentration in g/l is the concentration of remaining inorganic salts.

15
The concentrated brine is the aqueous solution comprising a VERY high concentration of inorganic salts which is obtained downstream of the membrane when a preconcentration stage (before a diafiltration-concentration stage) or a concentration stage alone is carried out.

20
The brine is the aqueous solution comprising a high concentration of inorganic salts which is obtained downstream of the membrane when a diafiltration stage followed by a concentration stage is carried out.

25 In the case of the reverse osmosis, the brine is the aqueous solution which remains upstream of the membrane and the purified water is the aqueous solution which has passed through the membrane. In both cases, the concentration is the concentration of inorganic salts.

No. of the experiments No.	Nanofiltration stage									Reverse osmosis stage		
	Pre-concentration	Diafiltration	Concentration	CC* -1 (g/l)	CB* -1 (g/l)	B* -1 (g/l)	DR (colorant) %	%NaCl	Reverse osmosis	CB* -1 (g/l)	PW* -1 (g/l)	%NaCl
1	no	Yes P=20 bar T=50°C A=400 l/h	yes	(1.98)		42.26 (12.46)	99.33		no			
2	no	Yes P=21 bar T=20°C A=400 l/h	yes	(25.08)		21.56 (18.36)	99.33		no			
3	no	Yes P=20 bar T=45°C A=380 l/h	no	(7.59)		8.87 (21.69)	99.21		no			

4	no	Yes P=20 bar A=350 l/h T=50°C	yes	(3.97)		28.54 (10)	99.21		no
5	no	yes	no				99.48		
6	no	yes	no				99.48		
7	no	Yes P=25 bar T=50°C A=330 l/h	no				99.48		
8	no	Yes P=10 bar T=50°C A=300 l/h	yes	1.4 (5.7)		39.8 (14)	99.21	98.55	no
9	no	Yes P=20 bar T=50°C A=300 l/h	yes	(2.39)		75.27 (3.63)	99.21		no
10	no	Yes P=10 bar T=50°C A=350 l/h	yes	1.155 (5.89)		38.8 (12.7)	99.33	98.82	no

11	no	Yes P=5 bar T=50°C A=350 l/h	yes	0.88 (6.14)		50.69 (11.5)	99.21	99.01	no
12	no	Yes P=10 bar T=50°C A=100 l/h	yes	1.99 (5.7)		54.42 (10.8)	99.21	97.88	no
13	no	Yes P=20 bar T=50°C A=300 l/h	yes	4.45 (5.55)		35.5 (18)	99.21	95.83	no
14	no	Yes P=10 bar T=50°C A=400 l/h	yes	3.23 (4.8)		54.66 (11)	99.21	98.61	no
15	no	Yes P=10 bar T=50°C A=330 l/h	yes	1.68 (8.03)		47.72 (11.65)	99.21	98.02	no

16	no	Yes P=10 bar T=50°C A=350 l/h	yes	1.11 (5.66)		48.6 (12.67)	100	99.05	no
17	Yes P=10 bar T=50°C A=350 l/h	no	no	1.732 (76.49)	15.545 (68.73)		100	91.27	no
18	Yes P=10 bar T=50°C A=350 l/h	no	no	1.91 (75.15)	16 (67.74)		100	90.19	no
19	no	Yes P=10 bar T=50°C A=300 l/h	yes	2.18 (19.39)		16.77	/	95.22	no
20	no	Yes P=10 bar T=50°C A=300 l/h	yes	2.18 (4.2)		45.29 (9.22)	99.21	97.94	no

21	no	Yes P=10 bar T=50°C A=300 l/h	yes	3.1 (4.47)		52.49 (17.19)	/	98.42	no
22	Yes P=20 bar T=40°C A=350 l/h	no	no	119.63 (81.51)	183 (76.78)		100	58.05	no
23		Yes P=20 bar T=50°C A=400 l/h	yes	1.68 (12.73)		32.86 (18.52)	100	99.05	no
24		Yes P=20 bar T=50°C A=300 l/h	yes	2.5 (13.35)		45.53 (25.62)	100	98.1	no
25		Yes P=20 bar T=50°C A=300 l/h	yes	3.1218 (7.71)		61.181 (20.3)	100	98.21	no

26	Yes P=20 bar T=50°C A=100 l/h	yes	1.582 (9.75)		83.79 (26.13)	100	99.31	no	
27	Yes P=20 bar T=50°C A=400 l/h	yes	2.075 (7.94)		60 (21.33)	100	98.72	no	
28	Yes P=20 bar T=50°C A=400 l/h	yes	2.17 (9.96)		58.55 (20.89)	100	98.51	no	
29	no	Yes P=20 bar T=45°C A=400 l/h	no	3.059 (67.2)	145.62 (62.77)		100	97.56	no
30	no	Yes P=20 bar T=50°C A=400 l/h	no	95 (53.64)	223.128 (54.78)		99.21	66.11	no

31	Yes P=20 bar T=50°C A=400 l/h	yes	2.91 (3.44)	75.276 (13)	99.21	98.96	no			
32							Yes P=50 bar T=38/45°C A=400 l/h	5.247 (57.36)	8.178 (2.26)	22.54
33							Yes P=50 bar T=38/45°C A=400 l/h	5.024 (57.44)	7.955 (1.37)	19.46
34							Yes P=50 bar T=38/45°C A=600 l/h	5.28 (57.97)	7.975 (1.046)	19.94

DR (Colorant): Degree of retention of the colorant. The degree of retention is defined by DC = (1-Cp/Co) × 100

Cp/Co: Ratio of the concentration in the permeate to the concentration in the solution upstream of the membrane, measured by absorbance

TABLE: Dyes used

Dye	Family
Drimarene Blue HF-B	DFP
Drimarene Blue HF-G	DFP
Drimarene Blue HF-RL	DFP
Drimarene Blue K-2RL	DFP
Drimarene Blue X-3LR	TCLP
Drimarene Yellow X-4RN	TCLP
Drimarene Yellow HF-R	DFP
Drimarene Yellow K-2R	DFP
Drimarene Black SN 150	VS
Drimarene Orange K-GL	DFP
Remazol Yellow RR	VS
Remazol Black B	VS
Remazol Red RB	VS
Drimarene Red CL-5B	bireactive VS-MCT
Drimarene Red HF-2B	DFP
Drimarene Red HF-G	DFP
Drimarene Red K-4BL	DFP
Drimarene Red K-8B	DFP
Drimarene Red X-6BN	TCLP

DFP = difluoropyrimidine
5   TCLP = trichloropyrimidine
MCT = monochlorotriazine
VS = vinyl sulphone

Drimagen E2R is a chemical dyeing product, an aromatic sulphonated derivative.
10   Sandopur R3C is a chemical dyeing product, a copolymer of partially neutralized carboxylic acids

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CLAIMS

1. Process for the treatment of baths for the exhaustion dyeing of cellulose fibres with reactive dyes comprising a prefiltration, then a neutralization, then a nanofiltration and then a reverse osmosis.

2. Process according to Claim 1, which is characterized in that the dye baths are industrial baths and in that they comprise hydrolysed reactive dyes which preferably belong to the trichloropyrimidine, difluoropyrimidine, difluoromonochloropyrimidine, monochlorotriazine and vinyl sulphone families.

3. Process according to Claim 1 or 2, which is characterized in that the prefiltration is carried out with a filter with a membrane having a preferred cutoff threshold of between 80 and 120 microns.

4. Process according to Claims 1 to 3, which is characterized in that the neutralization is carried out with acid, preferably hydrochloric acid, in the presence or absence of bubbling of air.

5. Process according to Claims 1 to 4, which is characterized in that, during the nanofiltration, the separation is carried out in an aqueous solution, on the one hand, of inorganic salts present at high concentrations, on the other hand, of hydrolysed reactive dyes having masses close to those of the cutoff threshold of the membrane.

6. Process according to Claim 5 which is characterized in that feed liquor is continuously introduced into a filtration module comprising a nanofiltration membrane under a positive pressure to provide a liquor which has passed through the membrane (permeate) and a liquor which has transited without passing through the membrane (retentate), the retentate being continuously directed to the feed tank.

7. Process according to Claim 5, which is characterized in that, during the nanofiltration, hydrolysed reactive dyes are concentrated upstream of the

membrane and inorganic salts are removed through the membrane via a concentration step.

8. Process according to Claim 5, which is characterized in that, during the nanofiltration, the concentration of hydrolysed reactive dyes upstream of the membrane is kept constant by addition of pure water and inorganic salts are removed through the membrane via a diafiltration step.

9. Process according to Claim 5, which is characterized in that the nanofiltration stage can operate
   (i) in a single step (concentration),
   (ii) in two steps (diafiltration-concentration), or
   (iii) in three steps (concentration-diafiltration-concentration),
   preferably in three steps.

10. Process according to Claim 5, which is characterized in that the initial concentration of inorganic salts is between 30 and 100 g/l.

11. Process according to Claims 1 to 10, which is characterized in that, in the reverse osmosis step, the feed liquor has an initial concentration of inorganic salts of between 5 and 70 g/l , preferably between 10 and 15 g/l.

12. Process according to Claims 1 to 10, which is characterized in that the retentate from the reverse osmosis is composed of pure water comprising inorganic salts concentrated to between 3 and 8% by weight, without coloured waste products, at a pH preferably of between 5.5 and 6, and in that it can be reused in dyeing.
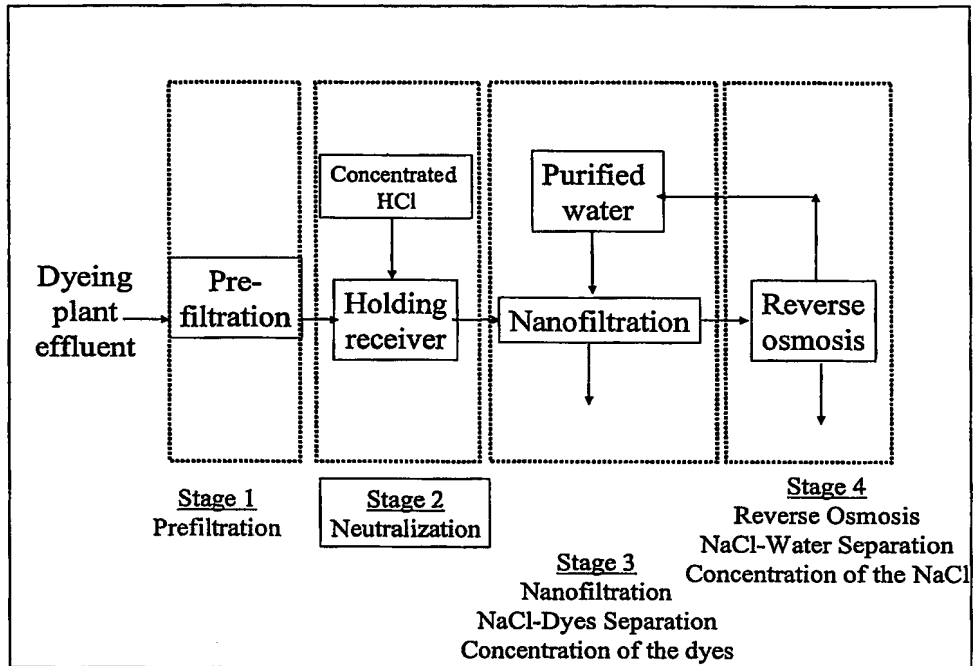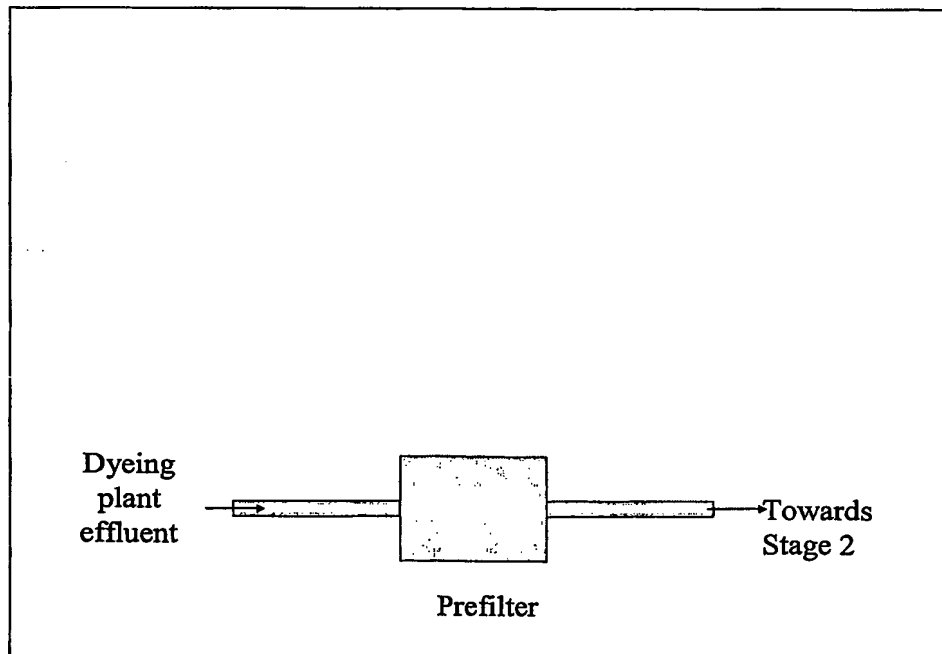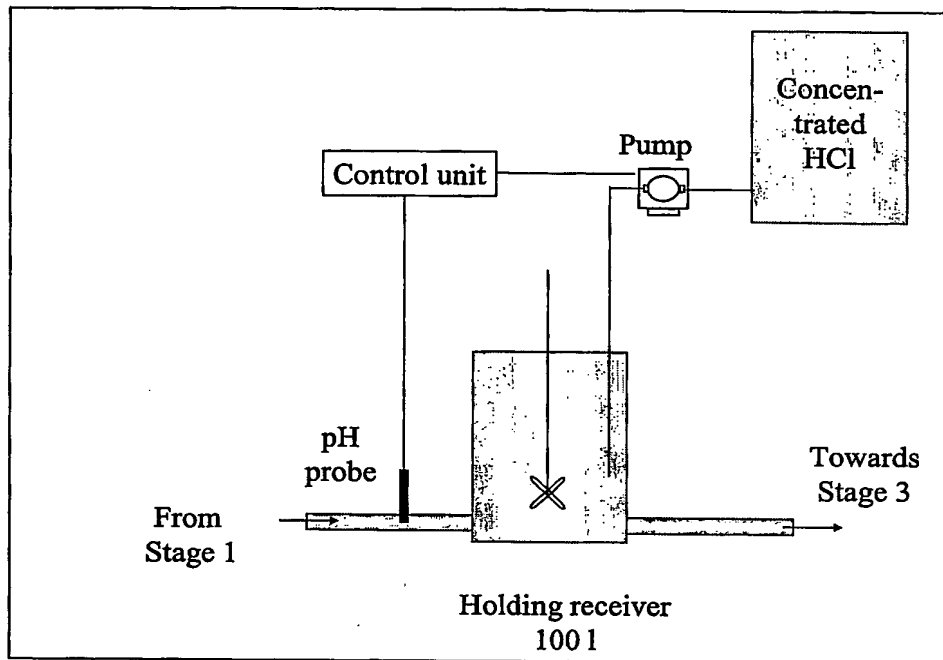
1 / 3

Figure 1

5

Figure 2

Figure 3
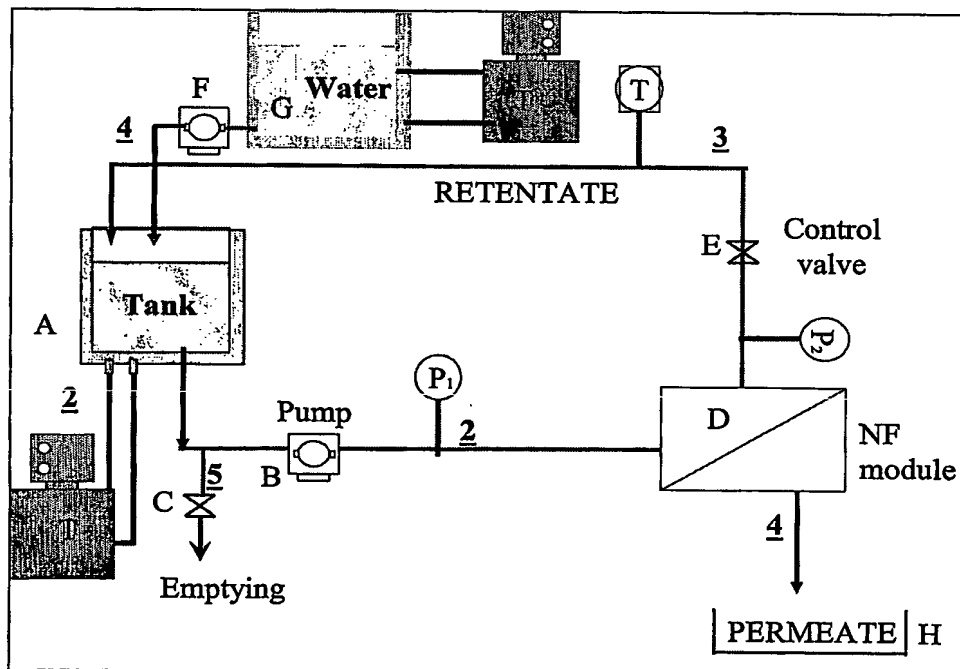
5

Figure 4

3 / 3
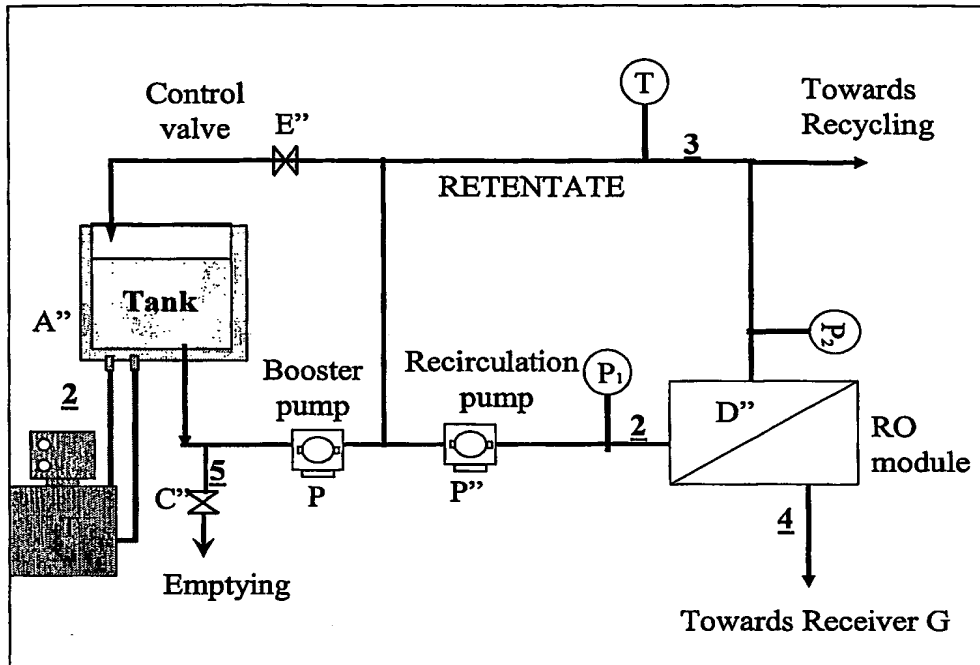
Figure 5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C09B67/00   B01D61/02   B01D61/58   C02F1/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C09B   B01D   C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 165 288 A (R.K.TEED ET AL) 21 August 1979 (1979-08-21) column 2, lines 44-68; claims	1-3,11
A	US 4 758 347 A (A.HENZ ET AL) 19 July 1988 (1988-07-19) claims 1,2; example	1,2,6,9, 11
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A	US 4 851 011 A (R.LACROIX ET AL) 25 July 1989 (1989-07-25) claims	1,9

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 January 2004	29/01/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Cordero Alvarez, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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